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(12) # EUROPEAN PATENT APPLICATION

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(54) **Process for the carbonylation of olefinically unsaturated compounds with a palladium catalyst.**

(57) Process for the carbonylation of an olefinically unsaturated compound with CO in the presence of water, an alcohol and/or a carboxylic acid and in the presence of a homogeneous catalytic system prepared by combining:-

a) a Pd(II) compound,

b) at least 5 mol of a triarylphosphine per gram atom Pd, and

c) at least 1 mol of a non-carboxylic acid having a $pK_a > 2$ and/or of a sterically hindered carboxylic acid having a $pK_a < 4.5$ per mol phosphine.

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PROCESS FOR THE CARBONYLATION OF OLEFINICALLY UNSATURATED COMPOUNDS WITH A PALLADIUM CATALYST

The invention relates to a process for the carbonylation of an olefinically unsaturated compound with carbon monoxide in the presence of water, an alcohol and/or a carboxylic acid.

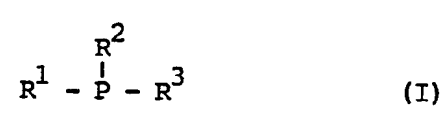
It is known from European Patent Application 106,379 that olefinically unsaturated compounds are carbonylated at a high reaction rate with carbon monoxide in the presence of water, an alcohol and/or a carboxylic acid, a palladium catalyst, at least 5 mol of a triarylphosphine per gram atom of palladium, and an acid having a pK_a below 2, except hydrohalogenic and carboxylic acids. Table B in said patent application shows that modifying this known process by using an acid having a pK_a higher than 2 (for example orthophosphoric acid or benzenephosphonic acid) or a carboxylic acid (for example trifluoroacetic acid or acetic acid) results in a low reaction rate.

It has now surprisingly been found that in the carbonylation of olefinically unsaturated compounds the reaction rate can be very much enhanced by the presence of an acid defined more closely hereinafter and of at least one mol of such an acid per mol of triarylphosphine.

Accordingly, the invention provides a process for the carbonylation of an olefinically unsaturated compound with carbon monoxide in the presence of water, an alcohol and/or a carboxylic acid, which process is carried out in the presence of a homogeneous catalytic system prepared by combining:-

a) a palladium(II) compound;

b) at least 5 mol of a phosphine of the general formula I



(I)

in which R^1, R^2 and R^3 each individually represent an optionally substituted aryl group, per gram atom of palladium, and

c) at least 1 mol of a non-carboxylic acid having a pK_a greater than 2 and/or of a sterically hindered carboxylic acid having a pK_a below 4.5, per mol of phosphine of the general formula I, the pK_a values measured at 18 °C in aqueous solution.

Examples of non-carboxylic acids having a pK_a greater than 2 and which are preferably used in the process according to the present invention are benzenephosphonic acid (pK_a = 2.5), 2-bromobenzenephosphonic acid (pK_a = 2.1) and orthophosphoric acid (pK_a = 2.1). Another example of such acids is arsenic acid.

The carboxylic acid must be sterically hindered which means that atoms or groups of atoms are present which interfere with one another, thus counteracting esterification of the acid. Examples of such acids are 2,4,6-trimethylbenzoic acid and 2,6-dimethylbenzoic acid. It is preferred to apply sterically hindered carboxylic acids having a pK_a -measured at 18 °C in aqueous solution -below 2. Among the sterically hindered carboxylic acids preference is given to the sterically hindered benzoic acids. Very good results have been obtained with 2,6-dichlorobenzoic acid (pK_a = 1.5). Other examples of sterically hindered benzoic acids are 2,6-difluorobenzoic acid, 2,4,6-trifluorobenzoic acid, 2,4,6-trichlorobenzoic acid, 2,6-dibromobenzoic acid, 2,4,6-tribromobenzoic acid, 2,6-diiodobenzoic acid and 2,4,6-triiodobenzoic acid. Modification of the process according to the present invention by replacing a sterically hindered carboxylic acid having a pK_a below 4.5 with a sterically hindered carboxylic acid having a pK_a above 4.5 results in an extremely low rate of carboxylation.

The upper limit for the molar ratio non-carboxylic acid having a pK_a greater than 2 and/or sterically hindered carboxylic acid to phosphine of the general formula I is not critical. This molar ratio is preferably not more than 50, but the use of molar ratios higher than 50, for example up to 150, is not excluded.

The olefinically unsaturated compound may be an unsubstituted or a substituted alkene or cycloalkene preferably having in the range of from 2 to 30, and in particular 2 to 20, carbon atoms and preferably in the range of from 1 to 3 double bonds. The alkene or cycloalkene may be substituted, for instance, with one or more halogen atoms or cyano, ester, alkoxy, hydroxyl, carboxyl or aryl groups. If the substituents are not inert under the reaction conditions, the carbonylation reaction may be accompanied with other reactions. For instance, the carbonylation of allyl alcohol is accompanied with esterification of the hydroxy group.

Examples of suitable olefinic compounds are ethene, propene, 1-butene, 2-butene, isobutene, the isomeric pentenes, hexenes, octenes and dodecenes, 1,5-cyclooctadiene, cyclododecene, 1,5,9-cyclododecatriene, allyl alcohol, methyl acrylate, ethyl acrylate, methyl methacrylate, acrylonitrile, acrylamide, N,N-dimethylacrylamide, vinyl chloride, allyl chloride, acrolein, oleic acid, methyl allyl ether and styrene.

The alcohols or carboxylic acids used in the process according to the invention may be aliphatic, cycloaliphatic or aromatic and may be substituted with one or more substituents, such as mentioned hereinbefore in connection with the olefinically unsaturated compounds to be used as starting material. The alcohol may therefore also be a phenol. The alcohols or carboxylic acids preferably contain not more than 20 carbon atoms. Examples of suitable alcohols or carboxylic acids are methanol, ethanol, propanol, isobutanol, tert-butyl alcohol, stearyl alcohol, benzyl alcohol, cyclohexanol, allyl alcohol, chlorocapryl alcohol, ethylene glycol, 1,2-propanediol, 1,4-butanediol, glycerol, polyethylene glycol, 1,6-hexanediol, phenol, cresol, acetic acid, propionic acid, butyric acid, caproic acid, trimethylacetic acid, benzoic acid, caprylic acid, succinic acid, adipic acid and hydroxycaproic acid. Special preference is given to alkanols and carboxylic acids having in the range of from 1 to 10 carbon atoms per molecule. If the alcohol or the carboxylic acid has more than one hydroxyl group or carboxyl group, different products may be formed, depending on the molar ratios existing between the reagents. For instance, depending on the quantity of olefinically unsaturated compound used, either a mono-ester or a diester may be produced from glycerol.

The process according to the present invention is particularly suitable for the preparation of methyl propionate, starting from ethylene, carbon monoxide and methanol.

The products formed in the process according to the invention may be further reacted if desired. For instance, the carbonylation of an olefin, when conducted in the presence of water, yields a carboxylic acid which, by reaction with a further quantity of olefin, may form an anhydride of a carboxylic acid. When the carbonylation is carried out in the presence of an alcohol, it yields an ester which, when water is present as well, may hydrolyze to form an acid and an alcohol, each of which may again react with an olefin. When the carbonylation is carried out in the presence of a carboxylic acid, it yields an anhydride of a carboxylic acid which, when water is present as well, may hydrolyze to form one or more carboxylic acids which in their turn may react with a further quantity of olefin.

Reaction of an alkanecarboxylic acid having n + 1 carbon atoms per molecule with an olefin having n carbon atoms per molecule yields the symmetrical anhydride of the alkanecarboxylic acid having n + 1 carbon atoms per molecule. This anhydride may optionally be hydrolyzed, half of the carboxylic acid formed may be collected as a product and the other half recycled to the carbonylation reactor. The process thus leads to the conversion of an olefin having n carbon atoms into a carboxylic acid having n + 1 carbon atoms.

Suitable homogeneous catalysts are the salts of palladium(II) with, for instance, nitric acid, sulphuric acid or alkanecarboxylic acids having not more than 12 carbon atoms per molecule. Salts of hydrohalogenic acids may, in principle, be used as well, but they have the drawback that the halogen ion may have a corrosive effect. A catalyst used by preference is palladium(II) acetate. Moreover, palladium complexes may be used, for instance palladium acetylacetonate, tetrakistriphenylphosphinepalladium, bis-tri-o-tolyl-phosphinepalladium acetate or bis-triphenylphosphinepalladium sulphate.

The quantity of palladium catalyst is not critical. Preference is given to the use of quantities in the range between 10^{-8} and 10^{-1} gram atom palladium per mol of olefinically unsaturated compound.

The substituted or unsubstituted aryl groups R^1, R^2 and R^3 of the phosphine $PR^1R^2R^3$ preferably contain not more than 18, in particular in the range of from 6 to 14 carbon atoms. Examples of suitable R^1, R^2 and R^3 groups are the naphthyl group and in particular the phenyl group. Suitable substituents are halogen atoms and alkyl, aryl, alkoxy, carboxy, carbalkoxy, acyl, trihalogenmethyl, cyano, dialkylamino, sulphonylalkyl and alkanoyloxy groups.

Examples of suitable phosphines are tri-p-tolylphosphine, tri-p-methoxyphenylphosphine, o-diphenylphosphinobenzoic acid and in particular triphenylphosphine. The phosphine is used in a quantity of at least 5 mol, preferably in the range of from 10 to 150 mol per gram atom of palladium. If the palladium catalyst already contains phosphine, this should be taken into account when calculating the amount of phosphine to be used.

In the process according to the invention the carbon monoxide may be used pure or diluted with an inert gas, such as nitrogen, noble gases or carbon dioxide. Generally the presence of more than 10 %v of hydrogen is undesirable, since under the reaction conditions it may cause hydrogenation of the olefinic compound. Generally preference is given to the use of carbon monoxide or a carbon monoxide-containing gas which contains less than 5 %v of hydrogen.

The carbonylation according to the invention is preferably carried out at a temperature in the range of from 50 to 200 °C, in particular 75 to 150 °C. The overall pressure preferably lies in the range of from 1 to 100, in particular 20 to 75, bar.

The molar ratio of the olefinically unsaturated compound to water, alcohol or carboxylic acid is not critical. The molar ratio between hydroxy groups and olefinic double bonds may lie for instance in the range of from 0.1 : 1 to 10 : 1. When using a mono-olefin and either water, a monohydric alcohol or a monobasic acid, preference is usually given to the use of an excess of the hydroxy compound mentioned. However, when using a polyhydric alcohol or a polybasic acid to prepare a polyester or a polyanhydride, it will generally be necessary to use an excess of olefinic compound.

The process according to the invention may be carried out batchwise, continuously or semi-continuously. Generally there is no need for the use of a solvent since usually there will be an excess of one of the reactants -for instance the alcohol -which may serve as a solvent as well. If required, however, a solvent may be used, for instance a sulphoxide such as dimethyl sulphoxide or diethyl sulphoxide; a sulphone such as diisopropyl sulphone or tetrahydrothiophene 1,1-dioxide (also referred to as "sulfolane"); ethers such as diethyl ether, tetrahydrofuran, 3,6-dioxaoctane (diethyl ether of diethylene glycol), methyl tert-butyl ether, 1,4-dioxane, anisole, 2,5,8-trioxanonane (dimethyl ether of diethylene glycol, also referred to as "diglyme"), diphenyl ether and diisopropyl ether; hydrocarbons such as hexane, cyclohexane, octane, benzene, toluene, o-xylene, m-xylene, p-xylene, ethylbenzene and cumene; halogenated hydrocarbons such as chloroform, 1,2-dichloroethane, perfluoroalkanes, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene; N,N-dialkyl substituted amides such as N,N-dimethylformamide and N-methylpyrrolidone; esters such as methyl propionate, ethyl acetate and methyl benzoate; nitro compounds such as nitrobenzene. The primary reaction product of the carbonylation reaction may also be used as a solvent.

The following Examples further illustrate the invention.

Example 1

A 300-ml magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) was charged with methanol (50 ml), palladium(II) acetate (0.1 mmol), triphenylphosphine (3 mmol) and orthophosphoric acid - (10 mmol). The autoclave was flushed with carbon monoxide, filled with ethylene until a pressure of 20 bar was obtained and then with carbon monoxide until a partial pressure thereof of 30 bar was obtained, sealed and heated to a temperature of 120 °C. The contents of the autoclave were analysed by gas-liquid chromatography; the reaction rate was 700 g methyl propionate per g palladium per hour.

Example 2

An experiment was carried out as described in Example 1, charging the autoclave with the following materials:-

methanol	50 ml	2,6-dichlorobenzoic acid	10 mmol
palladium(II) acetate	0.1 mmol	ethylene	20 bar
tri(p-methoxyphenyl) phosphine	2 mmol	carbon monoxide	30 bar

The reaction rate was 1000 g methyl propionate per g palladium per hour.

Example 3

An experiment was carried out as described in Example 1, charging the autoclave with the following materials:-

methanol	50 ml	benzenephosphonic acid	10 mmol
palladium(II) acetate	0.1 mmol	ethylene	20 bar
triphenylphosphine	2 mmol	carbon monoxide	30 bar

The reaction rate was 800 g methyl propionate per g palladium per hour.

Example 4

An experiment was carried out as described in Example 2 with the exception that 2,6-dichlorobenzoic acid (10 mmol) was replaced with 2,4,6-trimethylbenzoic acid (10 mmol, pK_a below 4.5).

The reaction rate was 400 g methyl propionate per g palladium per hour.

Comparative Experiment

An experiment was carried out as described in Example 2 with the exception that 2,6-dichlorobenzoic acid (10 mmol) was replaced with pivalic acid (10 mmol, $pK_a = 5.0$).

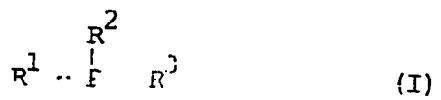
The reaction rate was less than 5 g methyl propionate per g palladium per hour.

Claims

1. A process for the carbonylation of an olefinically unsaturated compound with carbon monoxide in the presence of water, an alcohol and/or a carboxylic acid, which process is carried out in the presence of a homogeneous catalytic system prepared by combining:-

a) a palladium(II) compound;

b) at least 5 mol of a phosphine of the general formula I



(I)

in which R^1, R^2 and R^3 each individually represent an optionally substituted aryl group, per gram atom of palladium, and

c) at least 1 mol of a non-carboxylic acid having a pK_a greater than 2 and/or of a sterically hindered carboxylic acid having a pK_a below 4.5, per mol of phosphine of the general formula I, the pK_a values measured at 18 °C in aqueous solution.

2. A process as claimed in claim 1 in which the non-carboxylic acid is benzenephosphonic acid.

3. A process as claimed in claim 1 in which the non-carboxylic acid is orthophosphoric acid.

4. A process as claimed in any one of the preceding claims in which the sterically hindered carboxylic acid has a pK_a -measured at 18 °C in aqueous solution -below 2.

5. A process as claimed in any one of the preceding claims in which the sterically hindered carboxylic acid is a benzoic acid.

6. A process as claimed in claim 5 in which the benzoic acid is 2,6-dichlorobenzoic acid.

7. A process as claimed in any one of the preceding claims in which not more than 50 mol of said non-carboxylic acid and/or of said sterically hindered carboxylic acid are used per mol of said phosphine.

8. A process as claimed in any one of the preceding claims in which from 10 to 150 mol of said phosphine per gram atom of palladium are used.

9. A process as claimed in any one of the preceding claims in which the aryl groups represented by R^1, R^2 and R^3 in the general formula I have in the range of from 6 to 14 carbon atoms.

10. A process as claimed in any one of the preceding claims in which the aryl groups are phenyl groups.

11. A process as claimed in any one of the preceding claims in which the palladium(II) compound is a palladium(II) salt of an alkanoic acid having not more than 12 carbon atoms per molecule.

12. A process as claimed in claim 11 in which the palladium(II) compound in palladium(II) acetate.

13. A process as claimed in any one of the preceding claims which is carried out at a temperature in the range of from 50 °C to 200 °C.

14. A process as claimed in any one of the preceding claims which is carried out at a total pressure in the range of from 1 to 100 bar.

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EUROPEAN SEARCH REPORT

Application number

EP 87 20 0329

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,X	EP-A-0 190 473 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * abstract, claims 1-4, 8, 10, 11, 12, 14-17 *	1,2,4, 7,8-14	C 07 C 51/14 C 07 C 67/38 C 07 C 51/56 C 07 C 53/122 C 07 C 69/24 C 07 C 69/608
Y	GB-A-1 066 772 (BADISCHE ANILIN- & SODA-FABRIK) * page 3, lines 27, 95, 110-115; all claims *	1,11, 13,14	
Y	US-A-3 501 518 (N. VON KUTEPOW et al.) * abstract; column 11, example 22; claims 1-4 *	1	
Y	EP-A-0 055 875 (SHELL INTERNATIONALE RESEARCH) * MAATSCHAPPIJ B.V. abstract; claims 1-9, 11; page 3, lines 23-26; page 5, lines 23-24 *	1,11-13	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 07 C 51/00 C 07 C 67/00 C 07 C 53/00 C 07 C 69/00
Y,D	EP-A-0 106 379 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * abstract; claims 1-4, 7-14 *	1,2,8-10,13,14	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	21-05-1987	RUFET J.M.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A,P	EP-A-0 186 228 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * abstract, claims 1-10, 12, 14-20, 22-24, 26, 27 *	1-4,7-14	
A,P	EP-A-0 198 521 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * abstract, claims 1-3, 5, 10-15 *	1,8-14	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)

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